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A11101295006

/Bulletin of the Bureau of Standards
QC1 .U5 V13;1916-17 C.2 NBS-PUB-C 1905



RELATION BETWEEN COMPOSITION AND DENSITY OF AQUEOUS SOLUTIONS OF COPPER SULPHATE AND SULPHURIC ACID

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I. INTRODUCTION

In connection with an investigation on the regulation of solutions for electrodeposition, especially of acid copper sulphate solutions for electrotyping, it was found desirable to devise a simple method of determining and adjusting their composition. Since the solutions usually employed for the above purpose contain only copper sulphate and sulphuric acid, the composition of any given solution is fixed if the acid content and density at a given temperature are known. The density can be readily determined with a hydrometer, and the acidity can be ascertained with sufficient accuracy by titration with standard alkali, using methyl orange as indicator, as described by Wogrinz.¹ In order, therefore, to learn the content of copper sulphate, all that is required is a table showing the density of solutions containing known amounts of copper sulphate and of sulphuric acid.

Although the densities of solutions of copper sulphate and of sulphuric acid have been determined separately, no systematic study of the densities of solutions containing both could be found in the literature. Only in isolated cases were such data given concerning certain baths, such as those recommended by Pfauhauser,² Langbein-Brannt,³ Steinach and Buchner,⁴ and others.

The concentration of solutions containing both copper sulphate and sulphuric acid is limited by the fact that addition of sulphuric

¹ Chem. Ztg., **37**, p. 869; 1913.

² Electrodeposition of Metals, 7th ed., p. 574-575, 590; 1913.

³ Die Galvanoplastik, p. 37-38; 1904.

⁴ Die Galvanische Metallniederschläge, p. 160-161; 1911.

acid to copper sulphate solution causes a marked decrease in the solubility of the copper sulphate. Thus, while 395 grams of crystallized copper sulphate is contained in 1 liter of the saturated solution at 15° C, the addition of 100 grams per liter of sulphuric acid reduces the solubility of the copper sulphate to 215 grams per liter. Since in any practical work it is necessary to use solutions somewhat removed from the saturation point, the actual field is probably included in the range of 0 to 20 per cent of each of the constituents. Such solutions, therefore, formed the basis of this investigation. The temperature range of 25° to 40° C was selected as including the normal temperature employed in most copper plating or refining operations. Doubtless the expansion coefficients determined from such data will permit extrapolation over a moderate range above and below the temperatures used.

II. METHOD OF INVESTIGATION

1. PREPARATION OF SOLUTIONS

In order to avoid the influence of temperature in the preparation of the solutions, they were all made of a known composition by weight, expressed in grams of each constituent per kilogram of solution. They were prepared in duplicate by mixing accurately weighed portions of water and of standardized concentrated solutions of copper sulphate and of sulphuric acid.

The stock sulphuric acid solution was prepared by diluting c. p. acid to about 12 normal with distilled water, and was standardized by the barium sulphate method with the usual precautions. It was also compared with a hydrochloric acid solution, standardized by silver chloride precipitation, through a solution of sodium hydroxide, using methyl orange as indicator.

The concentration of the sulphuric acid solution as determined by the barium sulphate method agreed with that obtained by comparison with the standard hydrochloric acid solution to within about 1 part in 1500. Weight burettes were used, the individual titrations agreeing to within less than 1 part in 2000.

The solution of copper sulphate was prepared from recrystallized salt, which gave a perfectly clear solution. The concentration of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was calculated from the copper content determined electrolytically, the greatest difference between any two results being 1 part in 3000. Complete removal of copper from the electrolyte was confirmed by testing with $\text{K}_4\text{Fe}(\text{CN})_6$.

2. DENSITY DETERMINATION

Method of Determination.—The density measurements were made by the method of hydrostatic weighing, i. e., by weighing in the sample under investigation a sinker of known mass and volume. The density⁵ of the liquid is then calculated by means of the equation:

$$D_t = \frac{W - \frac{(w - w_1) + (w - w_2)}{2} \left(1 - \frac{\rho}{8.4}\right)}{V_t}$$

in which

D_t = Density at temp. t

W = Mass of sinker in vacuo

w = Weighings with sinker off

w_1 and w_2 = Weighings with sinker on

ρ = Air density

8.4 = Assumed density of brass weights

V_t = Volume of sinker at temp. t

Apparatus Used.—The apparatus used is described in detail in Bureau publications (Technologic Paper No. 9 (1912) and Bureau of Standards Bulletin, Vol. 9, pp. 371-378 (1913)). A short description of the apparatus is given, as follows:

The densimeter tube (about 45 cm long and 2.5 cm in diameter) containing the sample is placed in a water bath which is kept in constant circulation. This bath is surrounded by another, also in circulation, the temperature of which is regulated by means of an electric heating coil and a brine cooling coil. The temperature of the inner bath is determined by the use of two mercury thermometers. The large sinker having a length of approximately 33 cm and diameter of 1.3 cm is attached below a small sinker and both are suspended by means of a wire from one arm of a sensitive balance. The small sinker which is in the liquid at all times serves the purpose of keeping the suspension wire taut and in position, and thus the effect of surface tension is eliminated.

Method of Making Observations.—After sufficient time has elapsed for attaining temperature equilibrium at the desired temperature, the first weighing is made with the large sinker attached, and the temperature is immediately read from each of the thermometers. Then the second weighing is made with the large sinker detached from the small sinker. In order to obviate

⁵ Throughout this paper the term "density" is used to denote mass per unit volume and is here expressed in grams per milliliter. The densities are therefore numerically the same as specific gravities in terms of water at 4° C as unity.

any correction for a possible change in temperature, the first weighing is repeated and the thermometers reread. The average of the temperatures at the two weighings is taken as the true temperature. The difference between the mean of these two weighings and the second weighing is the apparent weight of the large sinker in the sample at the given temperature. After completing the observations at one point, the temperature is changed to the next and the process is repeated in the same order.

III. RESULTS OF INVESTIGATION

The results of the density determinations and composition of the samples are shown in Table 1.

TABLE 1
Density of Copper Sulphate—Sulphuric Acid Solutions

CuSO ₄ ·5H ₂ O, g/kg	CuSO ₄ , g/kg	H ₂ SO ₄ , g/kg	Density, ^a 25° C	Mean density, 25° C	Density, 40° C	Mean density, 40° C	α ^b
50	31.97	0	1.03014		1.02489		
50	31.97	0	1.03017	1.03016	1.02488	1.02488	-0.00035
50	31.97	50	1.06297		1.05637		
50	31.97	50	1.06309	1.06303	1.05639	1.05638	- .00044
50	31.97	100	1.09843		1.09060		
50	31.97	100	1.09843	1.09843	1.09060	1.09060	- .00052
50	31.97	150	1.13552		1.12669		
50	31.97	150	1.13546	1.13549	1.12667	1.12668	- .00059
50	31.97	200	1.17421		1.16453		
50	31.97	200	1.17412	1.17416	1.16452	1.16452	- .00064
100	63.94	0	1.06454		1.05871		
100	63.94	0	1.06456	1.06455	1.05874	1.05872	- .00039
100	63.94	50	1.09835		1.09097		
100	63.94	50	1.09833	1.09834	1.09097	1.09097	- .00049
100	63.94	100	1.13497		1.12642		
100	63.94	100	1.13499	1.13498	1.12656	1.12649	- .00057
100	63.94	150	1.17367		1.16417		
100	63.94	150	1.17366	1.17356	1.16420	1.16418	- .00063
100	63.94	200	1.21399		1.20379		
100	63.94	200	1.21395	1.21397	1.20371	1.20375	- .00068
150	95.91	0	1.10062		1.09428		
150	95.91	0	1.10064	1.10063	1.09431	1.09430	- .00042
150	95.91	50	1.13555		1.12765		
150	95.91	50	1.13553	1.13554	1.12764	1.12764	- .00053
150	95.91	100	1.17366		1.16457		
150	95.91	100	1.17361	1.17364	1.16453	1.16455	- .00061
150	95.91	150	1.21392		1.20391		
150	95.91	150	1.21394	1.21393	1.20396	1.20394	- .00067
150	95.91	200			1.24528		
150	95.91	200	(c)		1.24518	1.24523	
200	127.9	0	1.13833		1.13152		
200	127.9	0	1.13835	1.13834	1.13154	1.13153	- .00045
200	127.9	50	(d)				
200	127.9	50	1.17485	1.17485	1.16638	1.16638	- .00056
200	127.9	100	1.21449		1.20476		
200	127.9	100	1.21447	1.21448	1.20475	1.20476	- .00065
200	127.9	150			1.24579		
200	127.9	150	(e)		1.24571	1.24575	

^a All densities here tabulated are expressed in grams per milliliter.

^b Change in density per degree rise in temperature.

^c Solutions of these compositions do not exist at 25° C.

^d Sample lost by breakage of the container.

In Table 1 the composition of the solutions is expressed in grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per kilogram of solution. The concentration in grams per liter may be readily obtained by multiplying the above concentrations in grams per kilogram by the corresponding densities. In each case density determinations were made upon duplicate solutions, and these results are seen to agree in most cases to somewhat better than 1 in the fourth decimal place. From the density data for 25° and 40° C, respectively, the thermal density coefficient α has been calculated, which may be defined as the change in density (always negative) for an increase in temperature of 1° C.

The above results are shown graphically in Fig. 1, which illustrates the effect upon the density of additions of copper sulphate to sulphuric acid solutions and of sulphuric acid to copper sulphate solutions. The curves for sulphuric acid solutions are derived from the data of Domke as given in Landolt and Börnstein, fourth edition (1912). The close agreement between the densities of solutions of the same total concentration, shown in Table 2, is

TABLE 2

Showing the Relation Between Total Concentration and Density

Total concentration, g/kg	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, g/kg	H_2SO_4 , g/kg	Density, 25° C
50	0	50	1.0300
	50	0	1.0302
100	0	100	1.0640
	50	50	1.0630
	100	0	1.0646
150	0	150	1.0994
	50	100	1.0984
	100	50	1.0983
	150	0	1.1006
200	0	200	1.1365
	50	150	1.1355
	100	100	1.1350
	150	50	1.1355
	200	0	1.1383
250	0	250	1.1751
	50	200	1.1742
	100	150	1.1737
	150	100	1.1736
	200	50	1.1749
300	0	300	1.2150
	100	200	1.2140
	150	150	1.2139
	200	100	1.2145

illustrated in Fig. 1. The curves passing through the circles show the change in density produced by the addition of copper sulphate to solutions containing a definite amount of sulphuric acid per kilo-

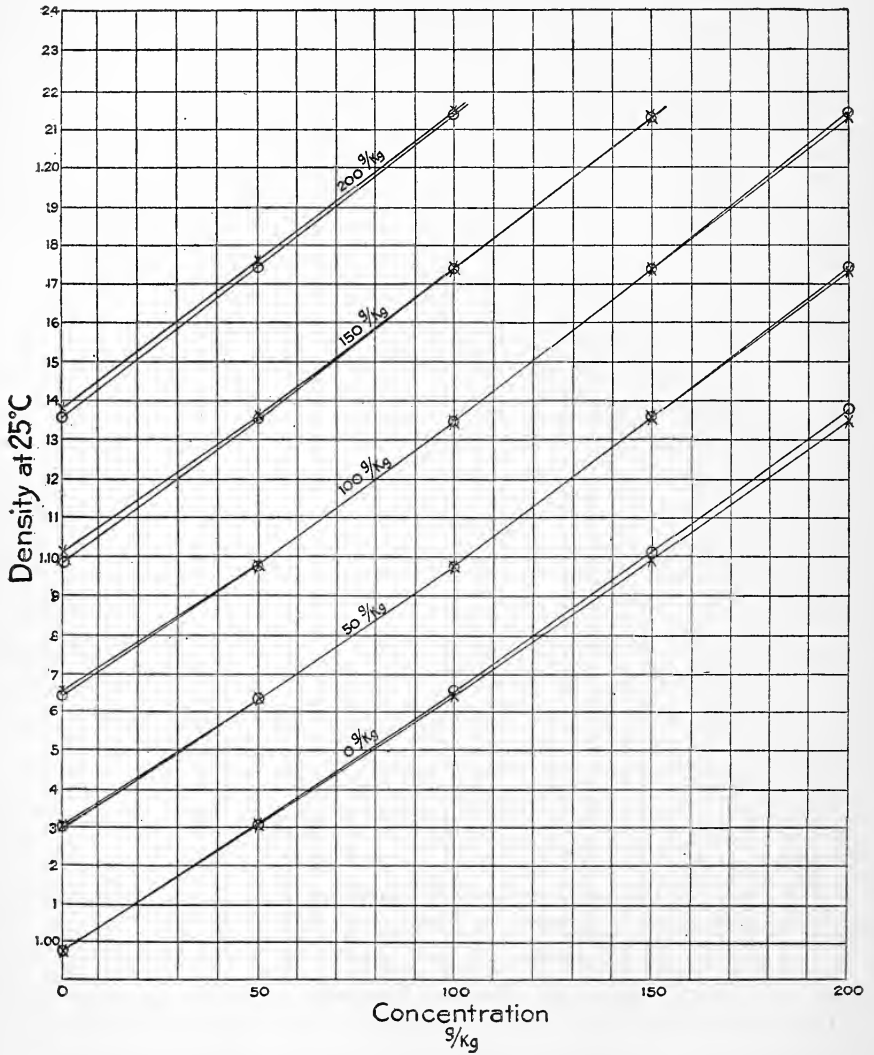


FIG. 1.—Density of copper sulphate-sulphuric acid solutions,
O—Sulphuric acid constant
X—Copper sulphate constant

gram of solution. Those through the crosses show the change in density produced by the addition of sulphuric acid to solutions containing a definite amount of copper sulphate per kilogram of solution, the total concentration in each case being the same as for the corresponding curve through the circles.

Example.—In the case of the curves marked 50 g/kg, the one passing through the circles shows the change in density produced by the addition of definite amounts (50, 100, 150, 200 grams) of copper sulphate to a solution containing 50 grams of sulphuric acid per kilogram of solution, and the one passing through the crosses shows the change in density produced by the addition of the same definite amounts of sulphuric acid to a solution containing 50 grams of copper sulphate per kilogram of solution.

From the above tables and curves it may be seen that—

1. Within the range studied, the density of copper sulphate-sulphuric acid solutions is approximately a linear function of the concentration.

2. The density of solutions of equal (not equivalent) concentrations of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and of sulphuric acid is nearly identical.

3. As a natural consequence of the conclusions noted in (1) and (2), a curious relation was found to exist, i. e., that the density of solutions containing appreciable amounts of each constituent is dependent principally upon the total concentration of the two solutes, and is almost independent of their proportion. (See Table 2.) Thus, a solution containing 50 grams per kilogram of copper sulphate and 150 of sulphuric acid has practically the same density (1.1355) as has a solution containing 100 grams per kilogram of copper sulphate and 100 of sulphuric acid (1.1350). This simple relation, which is apparently only a mathematical coincidence, has been used as the basis for the curve shown in Fig. 2 in which the total concentration, in grams per liter,⁶ of copper sulphate plus sulphuric acid is plotted against the density, yielding an almost straight line. The application of such a curve, or of the table derived from it (Table 3), in determining the composition of unknown solutions, is obvious, involving only a determination of the density and acidity, the latter then being deducted from the total concentration corresponding to the observed density, to obtain the copper sulphate concentration.

⁶ Obviously, the above relation exists whether the concentration is expressed in grams per kilogram or grams per liter. The data shown in Fig. 2 and Table 3 have been calculated to grams per liter since the results of the analysis of solutions are usually expressed in that form.

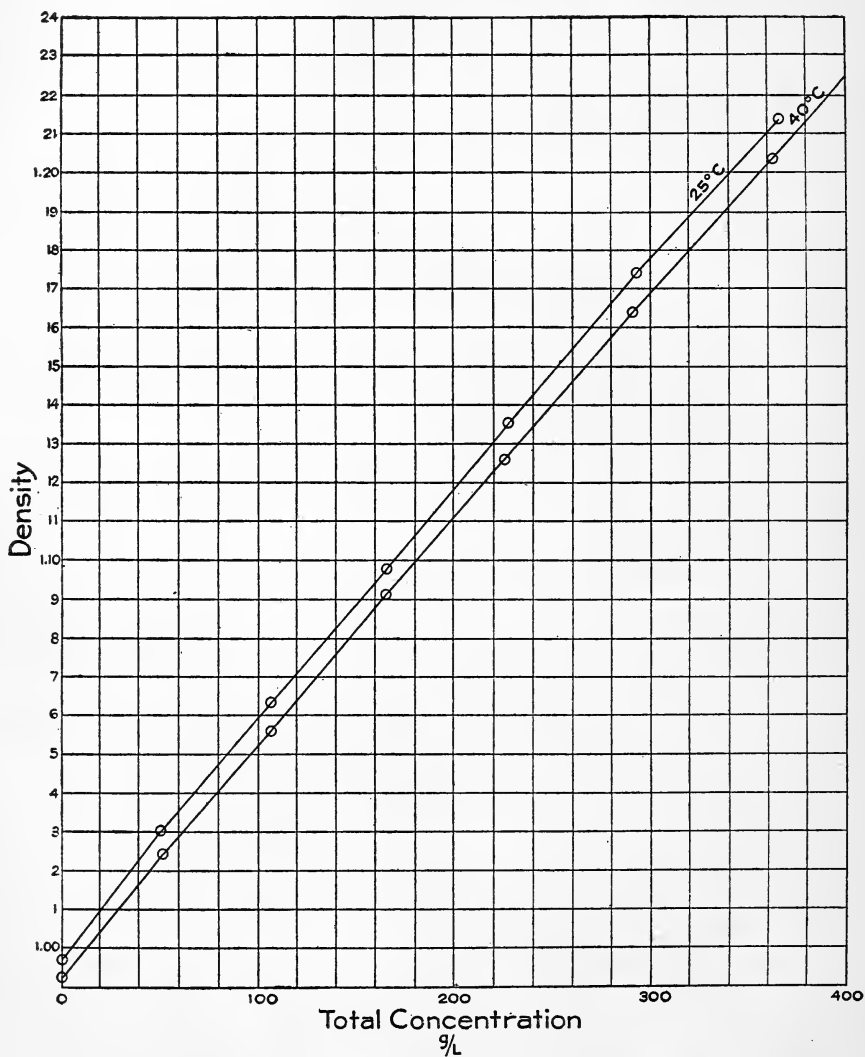


FIG. 2.—Density of solutions of total concentration of copper sulphate plus sulphuric acid

TABLE 3

Total Concentration of Solutions of Given Density

25° C		40° C	
Density	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + H_2SO_4 , g/l	Density	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + H_2SO_4 , g/l
1.01	20	1.01	26
1.02	36	1.02	43
1.03	52	1.03	60
1.04	68	1.04	76
1.05	84	1.05	93
1.06	100	1.06	110
1.07	117	1.07	127
1.08	133	1.08	144
1.09	150	1.09	161
1.10	166	1.10	178
1.11	183	1.11	195
1.12	200	1.12	212
1.13	217	1.13	229
1.14	234	1.14	247
1.15	251	1.15	265
1.16	268	1.16	282
1.17	286	1.17	300
1.18	303	1.18	318
1.19	321	1.19	336
1.20	339	1.20	354
1.21	357	1.21	372
1.22	375	1.22	390
1.23	393	1.23	408
		1.24	427

Details of the application of this table in the regulation of electrolytic copper baths will be given in the second edition of Bureau of Standards Circular 52.

This work was carried out under the direction of Messrs. W. Blum and H. W. Bearce.

WASHINGTON, November 27, 1915.





